IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IGB 1531

Applicant : Jeffrey Ronald KING; Karen TAYLOR; Simon Richard John LEGGETT; Stefan SCHÜTTEL; and Meinrad SCHAER

Serial No. : (Not yet assigned) Group Art Unit :

Filed : August 3, 2000 Examiner :

For : BISAZO DYES AND THEIR PREPARATION AND USE

E.19. 2/6/01 #2

Date: August 3, 2000

Assistant Commissioner for Patents
Washington, D.C. 20231

SUBMISSION OF PRIORITY DOCUMENT UNDER 37 C.F.R. §1.55(a)

Sir:

Applicants filed the present application claiming the benefit, under the conditions specified in 35 U.S.C. §119, of the filing date of prior Great Britain Patent application 9918265.1 filed August 4, 1999.

Applicant herein submits a certified copy of the priority application pusuant to 37 C.F.R. § 1.55(a).

Respectfully submitted,
Attorney for Applicants

By:

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Name DARA L. ONOFRIO

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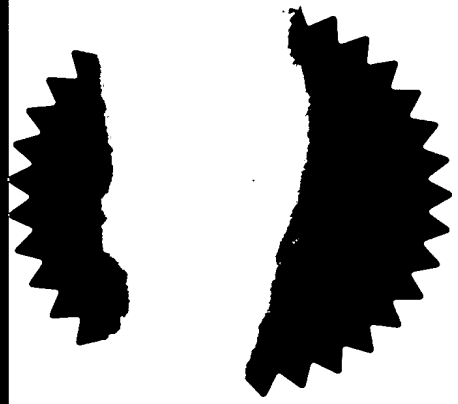

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Dated 8th June 2000

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The Patent Office

Cardiff Road
Newport
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04 AUG 1999

1. Your reference

IGB 1531

2. Patent application number
(The Patent Office will fill in this part)

9918265.1

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

ILFORD Imaging UK Limited
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and

ILFORD IMAGING Switzerland Gmbh, Route du L'Ancienne Papeterie, Case postale 160, CH-1723 Marly 1, Switzerland

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation

ILFORD UK Incorporated in UK 7654155005
ILFORD Switzerland Incorporated in Switzerlan

4. Title of the invention

Ink Jet Printing Method

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Dr W E Long
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Patents ADP number *(if you know it)*

511477002 7400856001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

Yes

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Description	11
Claim(s)	2
Abstract	1
Drawing(s)	1

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Priority documents	
Translations of priority documents	
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Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature R.L. Bottle Date 29/7/99

12. Name and daytime telephone number of person to contact in the United Kingdom W E Long 01565 650000

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Statement of inventorship and of right to grant of a patent

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The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference

IGB 1531

04 AUG 1999

2. Patent application number
(if you know it)

9918265.1

3. Full name of the or of each applicant

ILFORD Imaging UK Limited
Town Lane, Mobberley, Cheshire, WA16 7JL and
ILFORD Imaging Switzerland GmbH, Route de
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4. Title of the invention

Ink Jet Printing Method

5. State how the applicant(s) derived the right from the inventor(s) to be granted a patent

With regard to J R King, K Taylor, and S R J Leggett by the nature of their employment by ILFORD Imaging UK Limited, with regard to the other inventor by the nature of his employment by ILFORD Imaging Switzerland GmbH.

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(see note (c))

1

7. I/We believe that the person(s) named over the page *(and on any extra copies of this form)* is/are the inventor(s) of the invention which the above patent application relates to.

Signature W. R L

Date 29-7-99

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W E Long 01565 650000

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Enter the full names, addresses and postcodes of the inventors in the boxes and underline the surnames

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Statement of inventorship and of right to grant of a patent

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Newport
Gwent NP9 1RH

04 AUG 1999

1. Your reference

2. Patent application number
(if you know it)

9918265.1

3. Full name of the or of each applicant

4. Title of the invention

5. State how the applicant(s) derived the right from the inventor(s) to be granted a patent

6. How many, if any, additional Patents Forms 7/77 are attached to this form?
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7. I/We believe that the person(s) named over the page *(and on any extra copies of this form)* is/are the inventor(s) of the invention which the above patent application relates to.

Signature Date

8. Name and daytime telephone number of person to contact in the United Kingdom

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b) Write your answers in capital letters using black ink or you may type them.

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e) Once you have filled in the form you must remember to sign and date it.

Enter the full names, addresses and postcodes of the inventors in the boxes and underline the surnames

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7136470001

Patents ADP number *(if you know it)*:

Patents ADP number *(if you know it)*:

Patents ADP number *(if you know it)*:

Reminder

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New Patent Application

Applicants: ILFORD Imaging UK Limited

and

ILFORD Imaging Switzerland GmbH

Entitled: Ink Jet Printing Process

Case No: IGB 1531

This invention relates to a recording medium for ink jet recording and to the treatment of images prepared by an ink-jet printing process.

BACKGROUND of the INVENTION

Ink jet printing is a non impact printing method that in response to a digital signal produces droplets of ink that are deposited on a substrate to produce an image. Ink jet printing has found broad application in industry as well as for output from personal computers in the home and office. There is increasing interest in the use of digital imaging with ink jet printers as an alternative to conventional photographic imaging techniques. However the images produced by ink jet printers are seen as suffering several disadvantages when compared with conventional photographic images. In general they lack the overall quality of photographic images, look and feel substantially different, lack stability to light, and are more sensitive to water, scratching, rubbing, and environmental influences.

Aqueous inks are commonly used in ink jet printers for environmental and safety reasons, particularly those intended for use in the home or office. However sensitivity of the printed image to water is a particular problem where aqueous inks are used.

One way of overcoming these disadvantages is to laminate or encapsulate ink jet images, particularly those destined for external display. By lamination is meant the combination of a printed ink jet receiving layer with a transparent overlay, this combination usually being accomplished with an adhesive activated by heat, pressure, or both. The overlay acts as a physical protection for the image and completely seals it from ingress of water. By encapsulation is meant the combination of a printed ink jet receiving layer between two laminating sheets, that on the image surface being transparent, the combination being accomplished with an adhesive activated by heat, pressure, or both. Encapsulation is most effective if the laminating sheets extend beyond the ink jet image and are bonded to each other at the extremities, thus preventing ingress of water through exposed edges of the ink jet image.

However lamination and encapsulation both have disadvantages. They are expensive because additional materials are required together with additional handling and equipment. Moreover residual solvents such as the organic cosolvents which are frequently incorporated with aqueous inks remain trapped with the printed image, and these can sometimes degrade image quality by causing stain or migration of the image on storage or exposure. In addition the material of the laminate or adhesive can also deteriorate and cause stain on exposure. Laminates do not always adhere well to printed ink jet images, and adhesion can depend on the coatings of the ink receiving layer, the amount and type of solvent in the ink, and also on the quantity of ink laid

down. This is particularly found when the ink jet image is being used instead of a conventional photographic image, as heavy ink loads are often used to reproduce the image quality.

As an alternative to lamination, various additional coatings and treatments for ink jet receiving layers have been proposed. In most cases these are coatings such as lacquers or varnishes which have to be applied after printing the image, thus also requiring additional equipment. For instance our pending British Patent Application number 9810649.5 provides a method for increasing the rub resistance of an ink jet image by coating or over-printing the image with an aqueous solution of a styrene acrylate polymer.

Various types of ink jet receiving materials are also known wherein the top layer or an upper layer of the material comprises a film forming polymer and the lower layer or layers comprise ink receiving layers, such that when the image is printed the ink passes through the upper layer or layers and is held by the lower layers. The material is subsequently heated above the film forming temperature of the polymer, which thus fuses to form a barrier layer which seals the image. Such heat sealing systems are disclosed for instance in Japanese Patent Applications 59/222381, 07/237348, 08/02090, and 09/104164 and in European Patent Applications 0 858 905 and 0 858 906. This method is limited, however, as a high temperature is necessary to melt the polymer (170°C in the Examples of EP 0 858 906), and special equipment is

required to achieve this. Moreover not all substrates and ink receiving layers can withstand the high fusing temperature, and this restricts the generality of these methods. In addition the resultant image retains the solvents and can be subject to deterioration in the same fashion as a laminated or encapsulated image.

There is thus still a need for a convenient and general method for protecting ink jet images. We have found such a method.

SUMMARY of the INVENTION

According to the present invention there is provided an ink jet printing method which comprises the steps of:-

1) printing on to a receiving medium which comprises on a suitable substrate at least one ink receiving layer together with at least one upper protective layer which comprises particulate polymeric beads which are characterised by a film forming temperature of between 100° and 120° together with at least one hydrophilic binder, and

2) subsequently heating the printed image to form a stable image protecting coating.

In contrast to the materials previously known in the art, the image in the materials of this invention is substantially retained within the upper protective layer. It is believed, however, that any retained solvents are held in the lower image receiving layers, thus separating them from the colorant.

The protective layers of the invention are receptive to inks during printing, give high quality images of good colour strength, adhere well after printing and fusing, provide a high level of scratch and rub resistance to the final image even when wet, and maintain the same level of flexibility as the rest of the assembly.

DETAILED DESCRIPTION of the INVENTION

Suitable substrates to carry the layers of the invention include any of those commonly used for ink jet receiving media, for example paper, high wet-strength paper, treated paper such as resin or polyethylene coated paper, transparency materials, synthetic papers, and polymeric substrates such as cellulose acetates, polyesters, poly(propylene), and poly (vinyl chloride).

Suitable ink receiving layers include any of those commonly used in ink jet media, particularly those employing at least one hydrophilic binder such as gelatin, poly (vinyl alcohol), poly (vinyl pyrrolidone), carbohydrates such as gums, treated carbohydrates such as hydroxyethyl cellulose or carboxymethyl

cellulose, acrylic polymers, or mixtures of such binders. Such ink receiving layers are well known in the art. Preferably the ink receiving layer comprises poly (vinyl alcohol) having a degree of hydrolysis of at least 88% as binder. It is to be understood that the ink receiving layers for the materials of this invention may advantageously include additives which are commonly employed in ink jet receiving layers such as inorganic pigments or fillers such as silica, alumina, clays, and calcium carbonate, dye fixing agents such as cationic polymers, surfactants, cross linking agents, optical brighteners, and light stabilisers.

Suitable hydrophilic binders for the upper protective layer include poly (vinyl alcohol), copolymers of poly (vinyl alcohol), gelatin, poly (vinyl pyrrolidone), carbohydrates such as gums, treated carbohydrates such as hydroxyethyl cellulose or carboxymethyl cellulose, acrylic polymers, or mixtures of such binders. A preferred hydrophilic binder is poly (vinyl alcohol) which has a degree of hydrolysis of at least 90%, and a particularly preferred binder is poly (vinyl alcohol) which is about 99% hydrolysed. This is hereinafter referred to as 99%PVA.

A suitable particle size for the polymeric beads is between about 1 μm and about 50 μm, with a particle size between about 5 μm and about 20 μm being preferable. Suitable polymers for the polymeric beads include low density polyethylene and copolymers of ethylene with other ethylenically unsaturated

monomers, such as ethylene-acrylic acid copolymers. A particularly suitable particulate polymer comprises low density polyethylene spherical beads having an average diameter of about 12 μm. Another particularly suitable particulate polymer comprises spherical beads of a 7% acrylic acid/ polyethylene copolymer having an average diameter of about 10 μm. These polymers have melting points of 105-107°C.

A suitable coating weight for the upper protective layer is from about 15 to about 40 gm^{-2}. A preferred coating weight is between about 25 and about 30 gm^{-2}.

The upper protective layer may optionally also comprise additives such as surfactants to improve coating quality and cross linking agents such as aldehydes, boric acid, divalent metallic cations and the like.

The image receiving materials of the invention may be prepared by simultaneously coating the image receiving layer or layers together with the upper protective layer on to the substrate. Alternatively the upper protective layer may be coated on to a existing ink jet medium which comprises the substrate and image receiving layers. The upper protective layers of the invention are particularly suitable for this second aspect as they may be coated as aqueous formulations which give good adhesion to the image receiving layer.

According to one aspect of this invention, the printed image is heated by passing through a laminator. By laminator is meant a device which is normally used for the lamination of printed images which comprises a means of heating and pressing together the image and the laminating sheet thus causing the two to adhere, commonly by passing them through heated rollers. This aspect is particularly preferable because many printing and processing houses already possess and use laminators which can be applied to the materials of this invention. However the advantage of this invention is that the additional expensive lamination sheet is unnecessary.

According to another aspect of the invention, the printed image is heated by passing through a laminator in conjunction with a second, inert sheet which is held against the image protective layer of the material. The inert sheet does not adhere to the material, but protects it from the rollers of the laminator, and may be used to impart a high gloss or other desired appearance to the final image by suitable choice of the inert sheet. The inert sheet may then be recycled almost indefinitely.

The materials of the invention may be printed using any convenient ink jet printer, for example a continuous printer or a piezoelectric or thermal drop-on-demand printer. Suitable jetting inks include aqueous inks and those based on organic solvents such as 2-butanone (MEK) and mineral oils such as

those described in World Patent Application WO 96/24642. Suitable colorants for these inks include dyes or pigments. Preferred inks for the invention are pigmented aqueous inks.

The following Examples will serve to illustrate the invention:-

Example 1

A formulation was prepared using the following components:-

99% PVA 10% solution	10.0g
Silicone surfactant	0.25g
Ethylene acrylic acid copolymer beads	5.0g
Deionised water	4.75g

This formulation was coated on to a commercially available ink jet receiving medium which has a poly (vinyl chloride) substrate coated with a receiving layer comprising poly(vinyl alcohol)/ poly(vinyl acetate), silica, and a carbohydrate gum. The coating weight of the upper protective layer is 29 gm^{-2}. A test pattern was printed with pigmented inks using an Epson 200 printer, allowed to dry, and the coating was sealed by passing it through a GBC 1200 laminator at a heat setting corresponding to a temperature of 120° with the image face contacted with a smooth inert cover sheet. A clear glossy image was produced, resistant to wet rubbing, and the cover sheet was recovered for re use.

Example 2

A receiving layer was prepared as in Example 1. This was printed on a Novajet III printer and sealed using a Seal Image 600 laminator. A bright image was produced, resistant to smudging when rubbed with a thumb despite a high ink loading.

Example 3

A receiving layer was prepared as in Example 2. It was printed with a test chart and the image was sealed as in Example 2. A black area of the image showing 100% density of yellow, magenta, and cyan inks was selected, and a cross section prepared using a microtone. This cross section was viewed on a microscope and is shown in Figure 1.

This figure clearly shows the top sealed layer 1, the lower receiving layer 2, and the poly(vinyl chloride) base 3. Substantially all of the black image is located in the top sealed layer 1.

Example 4

A coating solution was prepared as follows:-

12.5g of polyethylene beads were mixed with 12.5g of a 5% solution of Olin 10G surfactant and warmed to 40°. 6.25g of a 10% solution of a high isoelectric point gelatin was added, and the mixture made up to 50ml with water and dispersed with ultrasound for 5 minutes. This solution was coated and printed as in example 2.

The accompanying figure shows the cross section of Example 3, wherein 1 is the upper protective layer, 2 is the receiving layer, and 3 is the poly (vinyl chloride) base.

CLAIMS :-

1. An ink jet printing method which comprises the steps of:-

   1) printing on to a receiving medium which comprises on a suitable substrate at least one ink receiving layer together with at least one upper protective layer which comprises particulate polymeric beads which are characterised by a film forming temperature of between 100° and 120° together with at least one hydrophilic binder, and

   2) subsequently heating the printed image to form a stable image-protecting coating.

2. A method according to claim 1 wherein the printed image is heated to create the protecting coating using a laminator.

3. A method according to claim 2 wherein the printed image is heated to create the protecting coating using a laminator in contact with an inert sheet on the image face of the material.

4. A method according to any of claims 1 - 3 wherein the hydrophilic binder is polyvinyl alcohol.

5. A method according to any of claims 1 - 3 wherein the particulate polymer comprises low density polyethylene.

6. A method according to claim 5 wherein the particulate polymer comprises low density polyethylene spherical beads having an average diameter of about 12 μm.

7. A method according to any of claims 1 - 3 wherein the particulate polymer comprises beads of a 7% acrylic acid/ polyethylene copolymer.

8. A method according to claim 7 wherein the particulate polymer comprises beads of a 7% acrylic acid/ polyethylene copolymer having an average diameter of about 10 μm.

IGB 1531

ABSTRACT

Ink jet Printing Process

There is described an ink jet printing method which comprises the steps of:-

1) printing on to a receiving medium which comprises on a suitable substrate at least one ink receiving layer together with at least one upper protective layer which comprises particulate polymeric beads which are characterised by a film forming temperature of between 100° and 120° together with at least one hydrophilic binder, and

2) subsequently heating the printed image to form a stable image protecting coating.

The protective layers of the invention are receptive to inks during printing and provide high quality images of good colour strength. The image is substantially retained within the upper protective layer as shown in the cross section wherein 1 is the upper protective layer, 2 is the receiving layer, and 3 is the poly (vinyl chloride) base.

The printed image is preferably sealed by passing through a laminator.

Figure 1